

–Original Message–

On the calculation of molecular eigenfrequencies¹

By

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It has recently been shown, [5], that the course of the atomic heats of various elements and compounds can be represented by the function

$$c = \frac{3\mathcal{R}}{n} \cdot \sum_{\nu_i}^{\nu_n} \frac{\left(\frac{\beta\nu_i}{T}\right)^2 \cdot e^{\frac{\beta\nu_i}{T}}}{\left(e^{\frac{\beta\nu_i}{T}} - 1\right)^2} \quad (1)$$

proposed by EINSTEIN, [4], provided that one uses an empirical additive term, for which the function $\gamma T^{\frac{3}{2}}$ was chosen, which takes into account the work that is done during thermal expansion against the cohesive forces. Here $\mathcal{R}$ represents the gas constant, n is the number of different eigenfrequencies present, ν_i is one of the dedicated eigenfrequencies, T is the absolute temperature and β the quotient $\frac{h}{k}$ of PLANCK's radiation law ($= 4.799 \cdot 10^{-11}$). γ is a constant peculiar to every substance. The second term $\gamma T^{\frac{3}{2}}$ should be neglected in the following, since it is usually not very important: if this work against the cohesive forces is known in more detail later, one can easily introduce it back into the resulting equations. For some substances with more complicated molecules, several eigenfrequencies have to be assumed. On the other hand, it has been shown that for most elements, as well as for some simple inorganic compounds, only one eigenfrequency is necessary. The aim here is to investigate whether something can be said *a priori* about their size. It can be easily shown that at small oscillation amplitudes the forces that drive a particle back to its rest position are proportional to its distance from the former². This result is independent of the function by which the decrease in the force acting between two particles with distance is expressed. One can therefore set

$$m \frac{d^2x}{dt^2} = -\alpha x \quad (2)$$

¹From the physical-chemical Institute of the University of Berlin,
Some values calculated with Excel®

²For reasons of symmetry it follows that in a homogeneous monatomic body the forces $f(x) - f(x) = 0$ act on a particle in its rest position in the direction of the X axis. If the particle is removed from the rest position by the distance Δx , then the acting force, which can probably

where m is the mass of the particle, x its distance from its rest position, t the time and α means the elasticity coefficient, so to speak. The solution of Equation 2 reads:

$$x = A \cdot \cos \left(t \cdot \sqrt{\frac{\alpha}{m}} - \varepsilon \right), \quad (3)$$

i.e. the particle carries out sinusoidal oscillations with the frequency:

$$\nu = \frac{1}{2\pi} \cdot \sqrt{\frac{\alpha}{m}}. \quad (4)$$

If one now assumes that at the melting point the *vis viva* of the particles and thus the amplitude of the vibrations is so great that the atoms, or rather their spheres of action, collide directly, then, as with a gas, the energy is transmitted directly by collision and the entire equilibrium situation comes into motion. The temperature can now only be increased after the average kinetic energy of the translational movement of the equilibrium positions has become equal to the average kinetic energy of the atoms of a monatomic gas of the same temperature. This would lead us to expect a molecular heat of fusion of $\frac{3}{2}\mathcal{R}T$ if the liquid has not polymerized at all and if the substance is melted at constant volume. In terms of magnitude, this may well be true, but it would be going too far at this point to reshape the current theory of fluids according to the above points of view, although it can be improved, and to compare it with the facts; This is also completely unimportant for the further treatment of the task set above.

If one sets the atomic diameter or the diameter of the sphere of action $\sigma = r \cdot (1 - \varrho)$, where r is the distance between two neighboring atomic centers and ϱ is the distance of the surfaces from each other as a fraction of r , an atom must oscillate from the equilibrium position by the distance $\frac{r\varrho}{2}$ in order to touch the neighboring atom, which of course oscillates just as far: So when passing through the rest position, the following *vis viva* must be contained in it:

$$L = \int_0^{\frac{r\varrho}{2}} \alpha x \, dx = \frac{\alpha \varrho^2 r^2}{8} \quad (5)$$

be assumed to be continuous, is

$$\begin{aligned} & f(x - \Delta x) - f(x + \Delta x) \\ &= f(x) - \frac{\Delta x}{1!} f'(x) + \frac{\Delta^2 x}{2!} f''(x) - \frac{\Delta^3 x}{3!} f'''(x) + \dots \\ & \quad - f(x) - \frac{\Delta x}{1!} f'(x) - \frac{\Delta^2 x}{2!} f''(x) - \frac{\Delta^3 x}{3!} f'''(x) + \dots \\ &= -\Delta x \cdot \left\{ 2f'(x) + \frac{\Delta x^2}{2!} f'''(x) + \dots \right\}, \end{aligned}$$

i.e. the size of the acting force is proportional to the distance Δx of the particle out of its rest position, if one may ignore the second and higher even powers of Δx .

However, according to EINSTEIN's formula, when looking at a linear oscillation at the melting point T_s , the kinetic energy of an atom as it passes through the rest position is

$$L = \frac{\mathcal{R}}{N} \cdot \int_0^{T_s} \frac{\left(\frac{\beta\nu}{T}\right)^2 \cdot e^{\frac{\beta\nu}{T}}}{\left(e^{\frac{\beta\nu}{T}} - 1\right)^2} dT = \frac{\mathcal{R}}{N} \cdot \frac{\beta\nu}{\left(e^{\frac{\beta\nu}{T_s}} - 1\right)}, \quad (6)$$

where N is the number of atoms in gram-atom or molecules in gram-molecule, respectively. As mentioned before, the second term $\frac{2}{5}\gamma T^{\frac{5}{2}}$ is ignored here. It is also assumed that the course of atomic heat can be represented by a eigenfrequency. Neglecting the higher powers of $\frac{\beta\nu}{T_s}$ this gives

$$L = \frac{\mathcal{R}}{N} \cdot \left(T_s - \frac{\beta\nu}{2}\right). \quad (7)$$

So it is approximate

$$\frac{\mathcal{R}}{N} \cdot \left(T_s - \frac{\beta\nu}{2}\right) = \frac{\alpha \varrho^2 r^2}{8} \quad (8)$$

from which

$$\alpha = \frac{8\mathcal{R}}{\varrho^2 r^2 N} \cdot \left(T_s - \frac{\beta\nu}{2}\right) \quad (9)$$

follows. So the eigenfrequency is given by the equation

$$\nu = \frac{1}{2\pi} \cdot \sqrt{\frac{8\mathcal{R} \cdot \left(T_s - \frac{\beta\nu}{2}\right)}{\varrho^2 r^2 N m}}, \quad (10)$$

where m is the mass of an atom and therefore $Nm = M$ is the mass of one gram-atom or gram-molecule, respectively, of the vibrating particle. Solving for ν we get

$$\boxed{\nu = \frac{\sqrt{2\mathcal{R}}}{\pi \varrho} \cdot \sqrt{\frac{T_s}{Mr^2} - \frac{\mathcal{R}\beta}{2\pi^2 \varrho^2 r^2 M}}}. \quad (11)$$

This formula is very similar to one found empirically, [5].

$$\nu = \text{const.} \cdot \sqrt{\frac{T_s}{Ma}},$$

where a is the atomic volume or molecular volume, respectively; If one neglects the second relatively insignificant term in the theoretically derived formula and assumes ϱ to be the same for all bodies, then it follows

$$\nu = \text{const.} \cdot \sqrt{\frac{T_s}{M \cdot \sqrt[3]{a^2}}}.$$

The Equation 11 derived above can be reduced to a simpler form by introducing the density d under the assumption that the atoms are arranged tetrahedrally, which is probably true for most amorphous and many crystallized bodies. The distance between two neighboring atomic centers r is:

$$r = \sqrt[6]{2} \cdot \sqrt[3]{\frac{a}{N\sqrt{n^5}}}, \quad (12)$$

where n is the number of atoms in the molecule and the number of molecules in one mole is taken to be $6.02214076 \cdot 10^{23}$ ³. Because $a = \frac{M}{d}$, it follows for the mean eigenfrequency that

$$\nu = \frac{\sqrt{2\mathcal{R}}}{\pi \varrho} \cdot \sqrt{\frac{T_s N^{\frac{2}{3}} d^{\frac{2}{3}} n^{\frac{5}{3}}}{2^{\frac{1}{3}} M^{\frac{5}{3}}}} - \frac{\mathcal{R} \beta d^{\frac{2}{3}} N^{\frac{2}{3}} n^{\frac{5}{3}}}{2\pi^2 \varrho^2 M^{\frac{5}{3}}}. \quad (13)$$

Combining the constants we get

$$\begin{aligned} & \frac{\sqrt{2 \cdot 8.314462 \cdot 10^7 \cdot 602.214076^{\frac{2}{3}} \cdot 10^{14}}}{2^{\frac{1}{6}} \cdot \pi} \cdot \frac{T_s^{\frac{1}{2}} d^{\frac{1}{3}} n^{\frac{5}{6}}}{\varrho M^{\frac{5}{6}}} \\ & - \frac{8.314462 \cdot 10^7 \cdot 4.799 \cdot 10^{-11} \cdot 602.214076^{\frac{2}{3}} \cdot 10^{14}}{2^{\frac{4}{3}} \pi^2} \cdot \frac{d^{\frac{2}{3}} n^{\frac{5}{3}}}{\varrho^2 M^{\frac{5}{3}}} \\ & = 3.088 \cdot 10^{11} \cdot \frac{T_s^{\frac{1}{2}} d^{\frac{1}{3}} n^{\frac{5}{6}}}{\varrho M^{\frac{5}{6}}} - 1.144 \cdot 10^{12} \cdot \frac{d^{\frac{2}{3}} n^{\frac{5}{3}}}{\varrho^2 M^{\frac{5}{3}}} \end{aligned} \quad (14)$$

If one calculates the filling of the space from the dielectric constant according to the CLAUSIUS-MOSSOTTI theory, [1], one gets:

$$\varrho = \sqrt[3]{n} \cdot \left(1 - \sqrt[3]{\frac{3\sqrt{2}}{\pi}} \cdot \sqrt[3]{\frac{D-1}{D+2}} \right), \quad (15)$$

where D is the dielectric constant. The eigenfrequency can now be calculated in absolute measure from all known data. In order to show that the formula gives usable values, at least in terms of magnitude, the eigenfrequency of the fluorspar shall be calculated here. If the melting point is assumed to be 1418 °C, the density to be 3.18 g cm⁻³ and the dielectric constant to 6.81⁴, this results in

$$\begin{aligned} \varrho &= \sqrt[3]{3} \cdot \left(1 - 1.105 \cdot \sqrt[3]{\frac{D-1}{D+2}} \right) \\ &= 1.442 \cdot (1 - 0.9621) = 0.0546, \\ \nu &= 3.088 \cdot 10^{11} \cdot \frac{1418^{\frac{1}{2}} \cdot 3.18^{\frac{1}{3}} \cdot 3^{\frac{5}{6}}}{0.0546 \cdot 78.1^{\frac{5}{6}}} - 1.144 \cdot 10^{12} \cdot \frac{3.18^{\frac{2}{3}} \cdot 3^{\frac{5}{3}}}{0.0546^2 \cdot 78.1^{\frac{5}{3}}} \\ &= 20.70 \cdot 10^{12} - 3.625 \cdot 10^{12} = 17.07 \cdot 10^{12}. \end{aligned}$$

³According to https://en.wikipedia.org/wiki/Avogadro_constant

⁴Value according to Handbook of Chemistry and Physics, e.g. 82nd edition, CRC Press, 2001

which gives a residual radiation to be expected at $10000 \cdot \frac{3 \cdot 10^{10}}{17,07 \cdot 10^{12}} \text{ cm} = 17.57 \mu\text{m}^5$. In fact, such have been observed at $24.5 \mu\text{m}$. Table 3 gives some of the calculated and found values of ν for those substances for which the necessary data were available. The values of the dielectric constants available in the literature differ so greatly that the eigenfrequency was usually calculated using the largest and smallest value of the dielectric constant given.

Since the CLAUSIUS-MOSSOTTI theory certainly does not provide exact values for the filling of space y for non-round atoms and also the uncertainty of the values is proportional to the expression

$$1 - 1.105 \cdot \sqrt[3]{y}$$

whereby

$$1.105 \cdot \sqrt[3]{y}$$

is approximately 0.9, and since in a compound one can in any case assume that the atoms are arranged in a non-tetrahedral manner, the above agreement can be described as satisfactory. It has been shown that ϱ has almost the same value for many substances, especially metals. One can therefore, without making a very big mistake, neglect the correction term and calculate the eigenfrequency according to the formula

$$\nu = \text{const.} \cdot \sqrt{\frac{T_s}{M \cdot \sqrt[3]{a^2}}} \quad (16)$$

after the constant has been determined by inserting a known eigenfrequency. How well this is true for homologous salts is shown by the following Table 1 where the values, calculated and found using the above formula, of the residual radiation wavelengths of the alkali metal haloids determined so far are shown. The constant is calculated from the eigenfrequency of Sylvin (KCl) to give⁶:

$$4.941 \cdot 10^{12}.$$

The melting points used for the calculation are taken from the work of TAMMANN and HÜTTNER, [8]. The stated observed wavelengths come from the publication by RUBENS and HOLLNAGEL, [7].

The eigenfrequencies of a number of elements have been determined from the course of atomic heat⁷. The following Table 2 also shows that the values of ϱ can be set constant as a first approximation. ν is calculated according to the formula

$$\nu = 2.06 \cdot 10^{12} \cdot \sqrt{\frac{T_s}{M \cdot \sqrt[3]{a^2}}}. \quad (17)$$

⁵It is $\lambda = \frac{v}{\nu}$, where v is the velocity (of light) and ν is the (eigen)frequency.

⁶const. = $4.74 \cdot 10^{12} \cdot \left(\frac{770}{74.5 \cdot \left(\frac{74.5}{1.98} \right)^{2/3}} \right)^{-1}$; values according to Wikipedia and Handbook of Chemistry and Physics, e.g. 82nd edition, CRC Press, 2001

⁷Cf. LINDEMANN's forthcoming dissertation. Berlin

Substance	λ , calc.	λ , found		μ , on average
KCl	—	62.0	70.3	63.4
KBr	85.9	75.6	86.5	82.7
KJ	112.6	—	—	96.7
NaCl	49.2	46.9	53.6	49.9

Table 1: Residual radiation wavelengths of known alkali haloids

The values marked “ ν , found” were obtained by comparing Einstein’s function with all available measurements of atomic heat. Even if there can be no question of a strict agreement, it does seem to follow from the table that the space actually occupied by the atoms is approximately proportional to the atomic volume, as considerations of a completely different kind have long made probable.

On the other hand, the true atomic diameter or the true diameter of the spheres of action of the atoms in solid bodies can be calculated from the above points of view.

As Einstein pronounced, [3], it is very conceivable that non-charged vibrating particles are the carriers of heat in solid bodies. This seems to be the case according to recent research by Mr REINKOBER, [6], who examined diamond for residual radiation in the area in question, in that no residual radiation was found here. In the case of inorganic compounds, in which the electrical charges are located at least asymmetrical to the center of oscillation, the natural oscillations of the heat carriers can probably be detected optically. I am currently using measurements of atomic heat to investigate whether the course of atomic heat in bodies with a known eigenfrequency can be represented by Einstein’s formula, assuming the eigenfrequency found optically. The atomic heat of quartz can be satisfactorily reproduced by introducing the eigenfrequency, which produces the residual radiation at $21.7\mu\text{m}$. There is also a measurement of the atomic heat of NaCl between -78 and -188°C by Sir JAMES DEWAR, [2], which agrees with the atomic heat calculated from the residual radiations at $51.7\mu\text{m}$. The fact that both the optically detectable eigenfrequencies and the eigenfrequencies determined from the atomic heat can be calculated at least in terms of magnitude using the same formula suggests that in both cases these are the same oscillating structures.

What may also be interesting is the conclusion from the above considerations that as the temperature increases, the residual radiation of a substance must be shifted towards the ultra-red part of the spectrum in proportion to its linear expansion coefficient.

Finally, I would like to express my deepest gratitude to Professor NERNST for his continued interest in this work.

element	$\nu \cdot 10^{-12}$, found	$\nu \cdot 10^{-12}$, calc.
Bi	small	1.4
Pb	1.2	1.4
Sn	2.7	10.8
Cd	2.7	2.1
Sb	3.1	2.3
Pt	3.1	3.1
Ag	3.3	3.2
Zn	3.7	3.1
Mg	5.1	5.4
Cu	5.3	4.7
Al	6.8	5.6
Cr	7.2	5.9
J	2.7	1.4
S	5.5	3.0
Si	10.7	7.0
graphite	22.6	19.3
Diamond	27.3	20.8

Table 2: Eigenfrequencies of different elements

Substance	M	d	T_s	n	ϱ	D	$\nu \cdot 10^{-12}$, calc.	$\nu \cdot 10^{-12}$, found	deviation
KCl	74.5	1.98	770	2	0.1151	4.75	4.26	4.74	-10.1
					0.1068	4.94	4.56		-3.7
NaCl	58.5	2.17	801	2	0.0819	5.6	7.26	5.8	25.2
					0.0657	6.12	8.73		50.6
CaF ₂	78.1	3.18	1418	3	0.0577	6.7	16.36	12.3	33.0
					0.0517	6.92	17.83		44.9
SiO ₂	60.1	2.65	1713	3	0.1590	4.27	8.56	14.45	-40.7
					0.1166	5.06	11.39		-21.2
S	32.06	2.07	388	1	0.2663	2.24	1.54	5.6	-72.5
					0.1125	4.22	3.38		-39.7
Diamond	12	3.51	4700	1	0.0677	5.5	50.74	27.6	83.9
									on average 4.5

Table 3: Comparison of calculated and found eigenfrequencies

References

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